

portions of 50, 30, and 20, he thinks it no great violation of probability, to suppose that experiments affected with no error would, in fact, have given these integral results instead of the former decimal parts.

Mr. Smithson proceeds further to express his doubts, not only of the existence of quadruple, but even of strictly triple compounds. He believes that all combination whatever is binary, and is inclined to consider the present compound as consisting of equal parts of galena and fahlertz; the latter being also a binary compound of the sulphurets of antimony and of copper, in the proportion of three of the former to two of the latter.

The author next computes the proportion of the four ultimate elements; and these, being deduced from assumed simple fractions, are simply as the numbers 12, 25, 15, and 8. These, he remarks, are sexagesimal parts of this ore, as were those also which in a former paper he assigned to calamine.

When in that communication he offered a system founded on the results of his own experiments, he is apprehensive that he may have been supposed to be influenced, even unconsciously to himself, by a favourite theory; but the present case he thinks not liable to the same objection, since no fondness for theory affected the experiments of Mr. Hatchett, which nevertheless accord with its principles when viewed in a proper light.

Mr. Smithson, conceiving it established that chemical compounds consist of elements united in simple proportions by weight, observes, that greater accuracy is to be expected from correct theory than can be obtained in chemical experiments.

The principles of his theory require that simple ratios should always obtain in binary compounds; and he gives instances from the subjects of the foregoing experiments, which any chemist can, by careful repetition, confirm.

The ratios which he assigns to the compounds of lead are such, that two parts of lead make three of sulphate of lead, and five of lead make six of sulphate of lead. So also five of antimony make six of sulphuret, and three of antimony make four of powder of algaroth.

From the only crystalline form which Mr. Smithson believes to exist of the triple sulphuret, he infers that its primitive form is a cube, and not a tetrahedral prism, as stated by Count Bournon; and he observes, that the angles given by the Count are at variance with each other.

On Oxalic Acid. By Thomas Thomson, M.D. F.R.S. Ed. Communicated by Charles Hatchett, Esq. F.R.S. Read January 14, 1808. [*Phil. Trans.* 1808, p. 63.]

Though much important information has resulted respecting the *formation* of this acid, from the experiments of Hermbstadt, Westrumb, Berthollet, Fourcroy, and Vauquelin, the *properties* of it have been rather neglected since the original dissertation of Bergman, to whom

we are indebted for the first account of its properties. Dr. Thomson has in consequence undertaken a set of experiments, with the view of ascertaining various particulars respecting it.

Since the crystals of oxalic acid effloresce and lose a part of their weight when moderately heated, he endeavours to ascertain what portion of this loss was to be ascribed to water of crystallization, by uniting a known quantity of the acid with lime, by precipitation from a known solution of it in muriatic acid.

The quantity of acid employed weighed 58·3 grains; the oxalate of lime produced, when perfectly dried, weighed 72 grains. This oxalate being heated to redness, gave 49·5 carbonate of lime; and by a further exposure to a violent heat, yielded 27 pure lime, which being deducted from 72 oxalate, left 45 for dry oxalic acid, or $\frac{75}{100}$ of the quantity employed for saturation. The same experiment also gives

the proportion of acid to base in the oxalate of lime to be $\left\{ \begin{array}{l} 62\cdot5 \\ 37\cdot5; \\ 100\cdot0 \end{array} \right.$

a proportion which differs from that of Bergman, because he neglected to neutralize the acid from which the lime was precipitated, and which retained a part in solution.

To obviate any chance of error in so fundamental an experiment, Dr. Thomson thought it worth while to verify that analysis by a different mode of operating. A known quantity of acid having been precipitated by lime-water, he obtained a quantity of oxalate of lime that corresponded accurately with the foregoing estimate.

The oxalate of magnesia is very similar to that of lime, and is not sensibly dissolved by water; nevertheless, if a solution of oxalate of ammonia be poured into a solution of sulphate of magnesia, no precipitate is formed till after concentration by heat.

Oxalate of potash readily crystallizes in flat rhomboids, which dissolve in thrice their weight of water at 60°. This salt also combines with excess of acid, forming a superoxalate, long known by the name of Salt of Sorrel, very sparingly soluble in water. The potash in this salt, as Dr. Thomson remarks, contains very nearly the double of that quantity of acid which would be necessary barely to neutralize it.

Soda also forms, with this acid, a salt that readily crystallizes, and it is said to be capable of combining with excess of acid; but Dr. Thomson has not tried it.

The oxalate of ammonia is much less soluble than either of the preceding. Dr. Thomson having carefully examined, by direct saturation of oxalic acid, the proportions in which the acid and base unite to form the several earthy and alkaline oxalates, gives tables of them, adapted to various practical purposes; but having remarked that oxalate of strontian thus formed contained a larger quantity of the earth than was expected, he neutralized a known quantity of oxalic acid by ammonia, and with that compound made a precipitate from muriate of strontian. By this method of obtaining the compound, the same quantity of acid was found to have united with only half the quantity of strontian that had been contained in the former precipitate; a

proportion which he had before observed to take place in the super-oxalate and neutral oxalate of potash.

In the decomposition of these salts by heat, Dr. Thomson found the acid to be resolved into water, carbonic acid, carbonic oxide, carburetted hydrogen, and charcoal.

With the view of determining with precision the composition of oxalic acid, Dr. Thomson made choice of the oxalate of lime, of which 100 grains by distillation yielded 60 cubic inches of gas, consisting of carbonic acid gas and inflammable gas, in the proportion of 2 of the former to 7 of the latter. The inflammable gas also consisted of 2 parts, seven tenths being carbonic oxide, and three tenths carburetted hydrogen.

Hence if 160 grains of oxalate of lime, which contain 100 oxalic acid, be distilled, the products are, 59·53 carbonic acid, 24·28 inflammable air, 11·51 water, 4·68 charcoal: and as the constituents of these products are known, the ultimate elements are, 64·69 oxygen, 31·78 carbon, 3·53 hydrogen; which Dr. Thomson considers to be, 64 oxygen, 32 carbon, and 4 hydrogen.

In the analysis given of this acid by Fourcroy, as performed by Vauquelin and himself, the quantity of carbonic acid appears much too small; and Dr. Thomson is convinced their method must be erroneous, as the quantity of carbonic acid alone that is formed during distillation contains considerably more carbon than they assign to oxalic acid.

From the weights of the elements obtained from oxalic acid by chemical analysis, Dr. Thomson turns to views of a different nature, and hopes to arrive at a more intimate and accurate knowledge of the difference between this acid and other vegetable products consisting of the same ingredients, by attending to certain numerical relations of their elements to each other: and this relation is such, that if hydrogen be expressed by 1, the number which corresponds to carbon is 4·5, and oxygen 6. Azote, expressed according to the same scale, will be 5. The law observable in their union is this, that in all their compounds the proportions of these constituents may be always expressed by these numbers, or by small multiples of them; for instance,

	Oxyg.	Hydr.	Carb.	Azote.
Water consists of	6	1	—	—
Carbonic oxide	6	—	4·5	—
Carbonic acid	2 × 6	—	4·5	—
Carburetted hydrogen . .	—	2 × 1	4·5	—
Olefiant gas	—	1	4·5	—
Nitrous oxide	6	—	—	2 × 5
Nitrous gas	6	—	—	5
Nitrous acid	2 × 6	—	—	5

From the knowledge of this law, which was first observed by Mr. Dalton, it is difficult (says Dr. Thomson) to avoid concluding, with him, that the numbers above given represent the relative weights of a single atom of each of these elements; that they first unite atom

to atom ; but that they may also combine in the proportion of two or more particles of one sort with one of another.

Dr. Thomson observes, that the same law holds also with respect to salts, and that numbers may be affixed to each of the acids and to each of the bases ; which numbers, or their multiples, will represent them in all the combinations into which these bodies enter.

In this scale the particle of sulphuric acid is represented by 33, muriatic acid by 18, nitric acid by 17, carbonic acid by 17·5, barytes 67, lime 23, soda 24, ammonia 6.

From these data, and from the proportion in which oxalic acid has been found above to combine with several bases, Dr. Thomson assigns the number 39·5, which represents the particle of oxalic acid. Reverting next to the proportion of its elements, and to the weights of their respective atoms, he finds the integrant particle of oxalic acid to consist of 4 atoms of oxygen, 3 of carbon, and 2 of hydrogen ; the aggregate weights of which amount to the same number, 39·5, at which he had arrived by a different mode of estimation.

According to these proportions, 100 parts of oxalic acid will consist of its three elements, in the proportion of 61, 34 and 5, instead of 64, 32 and 4 ; numbers not exactly corresponding, but, in the estimation of Dr. Thomson, approaching sufficiently near to heighten the probability of the reasoning employed.

We may next conceive 3 particles of oxalic acid thus constituted to be decomposed at once, and to yield 4 particles of carbonic acid, 2 of carburetted hydrogen, and 2 of carbonic oxide, 3 of water, and 1 particle of charcoal ; and might thence expect 100 parts of acid to yield,

Carbonic acid	55·70,	instead of	59·53,	actually obtained.
Inflammable gas ..	28·64,	—	24·28,	—
Water	11·81,	—	11·51,	—
Charcoal	3·80,	—	4·68,	—

It is impossible, Dr. Thomson observes, to expect exact correspondence till the numbers representing the weights of the elementary atoms be ascertained with accuracy, instead of the round numbers which he has assumed, for the purpose of showing an approximation of the theoretic inferences to the results obtained by experiment.

In an analysis of sugar, which follows, by a series of experiments and of hypothetical reasoning, different from the experiments and reasoning of Lavoisier, Dr. Thomson nevertheless agrees with him, to great accuracy, in his results : and assuming 64 oxygen, 8 hydrogen, and 24 carbon, as the true elements, if these numbers be respectively divided by the weights of their single particles, the number of atoms of each which combine to form sugar are to each other as 5, 3, and 4 respectively.